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(54) **Production of silica**

(57) The controlled production of silicas by flame hydrolysis in which the thickening effect may be adjusted

independently of the specific BET-surface of the silica obtained is achieved by introducing additional steam either into the reaction mixture or into the reaction flame.

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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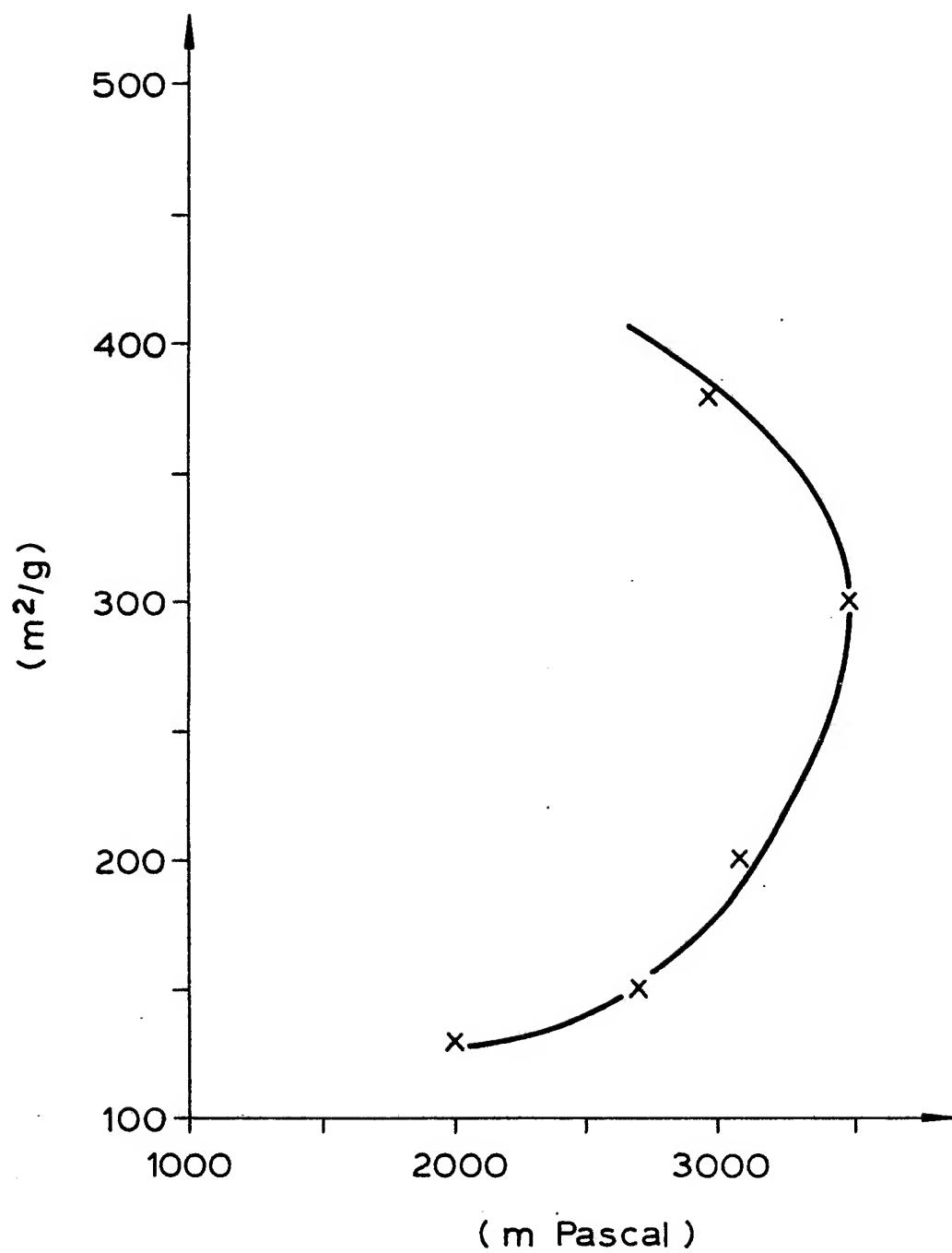


Fig . 1

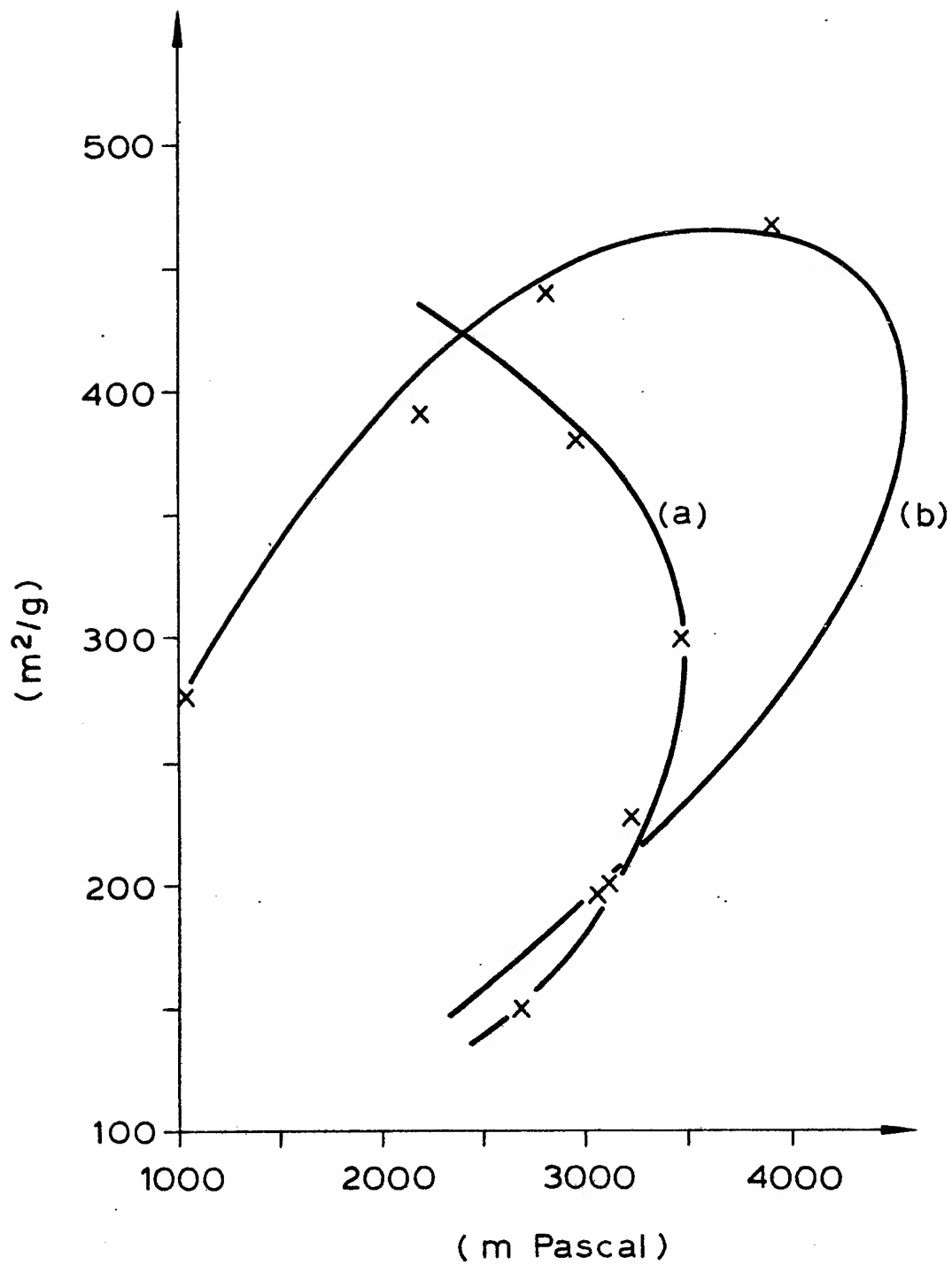


Fig . 2

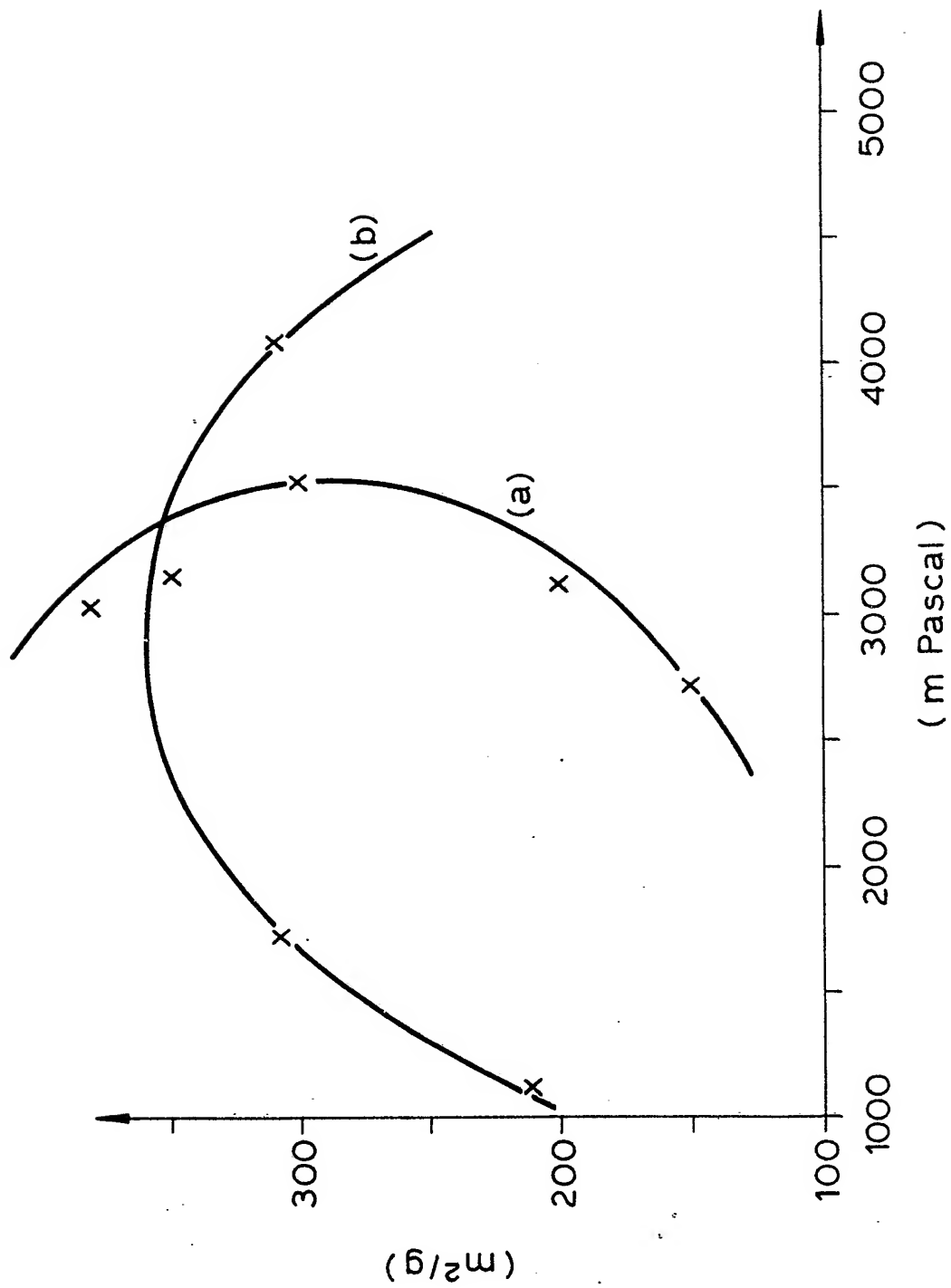


Fig . 3

## SPECIFICATION

**A process for the controlled production of silica by flame hydrolysis**

This invention relates to a process for the controlled production of silica by flame hydrolysis.

It is known that silica can be pyrogenically produced, for example by subjecting silicon  
 5 tetrachloride to flame hydrolysis. Silicas of this type are, for example, the various types of silica 5  
 commercially available under the name of Aerosil (Aerosil is a Trade Mark). They have different particle  
 sizes in the range from 7 to 40 nm and, accordingly, may be used for a variety of applications, for  
 example for thickening liquid systems.

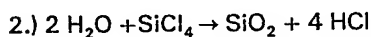
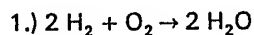
The typical characteristic quoted is normally not the particle size, but rather the specific surface in  
 10 m<sup>2</sup>/g, as measured by the BET-method. Providing the silicas in question are non-porous, these two 10  
 values correlate closely with one another.

Another equally important characteristic is the thickening effect of the various silicas in liquid  
 systems because most of these silicas are used as thickeners and thixotropic agents.

This characteristic is dependent upon the BET-surface so that, in the known silicas produced by  
 15 flame hydrolysis, a certain specific surface also means a certain thickening effect. 15

This correlation is illustrated in the graph in Figure 1 of the accompanying drawings.

In the known processes for the flame hydrolysis of silicon-hydrogen compounds in a hydrogen flame as  
 indicated by way of example below with reference to the hydrolysis of silicon tetrachloride), air or  
 oxygen, hydrogen and silicon tetrachloride are mixed and burnt in such a ratio to one another that, on  
 20 the one hand, the hydrogen can be completely burnt to form steam and, on the other hand, the silicon 20  
 tetrachloride is able to react quantitatively with the steam formed to form SiO<sub>2</sub>. The successive or  
 parallel reactions take place in accordance with equations 1, 2 and 3 below:



These equations also apply in cases where other silicon-halogen compounds are used as starting  
 material. Thus, it is possible to use volatile inorganic halogen compounds and/or organic halogen  
 compounds of silicon.

Suitable inorganic halogen compounds are, for example, SiHCl<sub>3</sub>, SiCl<sub>2</sub>H<sub>2</sub>, SiCl<sub>4</sub> whilst suitable  
 30 organic halogen compounds are, for example, CH<sub>3</sub>SiCl<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, SiCl<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub>—CH<sub>2</sub>—SiCl<sub>3</sub> or 30  
 (CH<sub>3</sub>—CH<sub>2</sub>)<sub>2</sub>SiCl<sub>2</sub>.

To carry out flame hydrolysis, the components hydrogen, oxygen or air and silicon tetrachloride are  
 delivered to a burner of the type diagrammatically illustrated in U.S. Patent No. 2,990,249 either  
 separately or in pre-mixed form and are burnt at the outlet opening of the burner. The quantity of  
 35 hydrogen is calculated in such a way that it is sufficient for quantitatively reacting the chlorine atoms on 35  
 the silicon atom to form hydrogen chloride, the reaction being accompanied by the formation of steam.  
 A small excess ensures that the reaction takes place not only quantitatively, but also sufficiently quickly.  
 The size of the hydrogen excess, based on the quantity of silicon tetrachloride, cannot be pitched at an  
 arbitrarily high level. Apart from the fact that this measure would add unnecessarily to the process  
 40 costs, limits are imposed on the size of the hydrogen excess by the fact that this reaction component 40  
 represents not only the component required for hydrolysis of the chloride, but also the energy donor.  
 The effect of an excessive increase in the hydrogen excess would be to increase the temperature of the  
 flame with adverse consequences for the quality of the SiO<sub>2</sub>-reaction products. It is possible to reduce  
 the reaction temperature by adding overstoichiometric quantities of air or oxygen to the reaction  
 45 mixture. This measure normally influences the reaction temperature and hence determines the fineness 45  
 or rather the specific surface of the reaction products. However, there are limits to this possibility  
 because the outflow velocity from the outlet opening of the burner has to remain within relatively  
 narrow limits so that any increase in the quantity of inert gas added reduces the performance of the  
 installation.

Now, the known process for producing silicas by flame hydrolysis according to U.S. Patent No., 50  
 2,990,249 is attended by the disadvantage that it is not possible to alter the correlation between  
 specific surface and thickening behaviour or to adjust the thickening effect of the silica independently of  
 the value of the specific surface.

The present invention relates to a process for the controlled production of silica by flame  
 55 hydrolysis in which an additional quantity of steam which does not result from the combustion of 55  
 hydrogen-containing gas required for flame hydrolysis is introduced into the reaction mixture.

The additional steam may be introduced in various ways. Thus, the additional steam may be  
 introduced into the mixing chamber of the burner through a separate pipe. In another preferred variant  
 of the process according to the invention, the additional steam may be introduced into the hydrogen-  
 60 containing gas or oxygen containing gas feed pipe leading to the burner so that a mixture of hydrogen 60

and steam or air and steam may be delivered to the burner. For mixing with steam, the hydrogen- or the oxygen-containing gas may be passed through a water evaporator at a temperature of from 20°C to the boiling temperature of the water.

In another preferred variant, the additional steam may be mixed with the gaseous silicon-halogen compound before it enters the burner, the temperature of the mixture of halogen silane having to be kept above the dew point in order to avoid deposits of silica. 5

In another preferred variant of the process according to the invention, the additional steam may even be introduced into the flame where the silica is actually formed. This may be done by means of a probe which is guided axially through the burner and allowed to project from the outlet opening thereof, or by means of an annular nozzle surrounding the flame. The only important requirement is that the additional steam should be mixed in as quickly and as homogeneously as possible to enable it to develop its full effect on the reaction and on the formation of the silica because the effect of the steam partial pressure decreases with the distance from the burner outlet. At the exit of the so-called flame tube, a heat-exchanger zone, into which the flame gases are normally introduced, the introduction of additional quantities of steam would not appear to have any further influence upon the property development of the silica. 10 15

The quantity of steam mixed in may be varied within wide limits.

The steam is preferably introduced at a temperature of from 150 to 250°C and under a pressure of from 10 to 20 atms. gauge, more particularly at a temperature of from 185 to 210°C and under a pressure of from 12 to 18 atms. gauge. 20

Any known inorganic and/or organic silicon-halogen compounds may be used as starting substances.

The ratio of steam to starting substance may be from 0.1 to 1 kg of steam kg of starting substance.

In another embodiment of the invention, a hydrocarbon for example may be used instead of pure hydrogen as the flame gas. Hydrocarbons suitable for this purpose are for example propane and/or butane. 25

An apparatus of the type illustrated in U.S. Patent No. 2,990,249 may be used as the burner. However, it is also possible to use a closed burner system in which no secondary air is able to enter the flame. 30

The controllability of the thickening effect is apparent for the accompanying drawings, wherein: Figure 1 illustrates the dependence of the thickening effect upon the BET-surface in known silicas.

Figure 2 illustrates the dependence of the thickening effect upon the quantity of steam introduced in correlation with the BET-surface in silicas produced by the process according to the invention, the additional steam being introduced into the reaction mixture before it enters the combustion chamber. 35

Figure 3 illustrates the dependence of the thickening effect upon the quantity of steam introduced in correlation with the BET-surface in silicas produced by the process according to the invention, the additional steam being introduced into the burner flame.

Figure 1 illustrates the dependence of the thickening effect upon the BET-surface in silicas produced by known processes in the form of a graph. The values for the individual silicas are as follows: 40

	Surface	Thickening	
	130 m <sup>2</sup> /g	2000 mPas	
	150 m <sup>2</sup> /g	2700 mPas	
	200 m <sup>2</sup> /g	3100 mPas	
45	300 m <sup>2</sup> /g	3500 mPas	45
	380 m <sup>2</sup> /g	3000 mPas	

The thickening values quoted above were determined from a polyester reference system.

This polyester reference system is prepared by mixing 80 parts by weight of Ludopal P 6 with 11.4 parts by weight of monostyrene and 7 parts by weight of styrene containing 1% of paraffin. This system is also used in all other determinations of the thickening effect. 50

According to Figure 2, the entire property spectrum, particularly the specific surface and the thickening behaviour, of the silicas obtained shifts with increasing quantity of steam introduced.

Thus, curve a) shows the correlation of specific BET-surface with the thickening behaviour of silicas as obtained in known processes by varying the excess of air. Accordingly, it is only possible by this measure to obtain a property combination of the silicas of the type already illustrated in Figure 1. 55

By contrast, curve b) show that, with increasing introduction of steam into the reaction mixture before combustion, both the thickening behaviour and also the specific BET-surface of the silicas obtained by the process according to the invention initially far exceed the values typical of the known

silicas according to curve a) by comparison with a basic setting before subsequently diminishing to a considerable extent with larger quantities of steam, new property combinations being obtained. For example, it is possible to produce silicas having the same BET-surface but vastly different thickening behaviour.

5 According to Figure 3, the entire property spectrum, particularly the specific BET-surface and the thickening behaviour, of the silicas obtained shifts with increasing quantity of steam introduced. 5

Thus, curve a) shows the correlation of specific BET-surface with the thickening behaviour of silicas as obtained in known processes by varying the excess of air. Accordingly, it is only possible by this measure, as already shown in Figures 1 and 2, to obtain a property combination in which the 10 thickening effect is dependent upon the specific BET-surface. 10

By contrast, curve b) shows that, with increasing introduction of steam into the flame, both the thickening behaviour and also the specific BET-surface of the silicas obtained by the process according to the invention are totally different from those of the known silicas according to curve a) by comparison with a basic setting. New property combinations may be obtained.

15 For example, it is possible to produce silicas having the same BET-surface but vastly different thickening behaviour. 15

The process according to the invention is illustrated by the following Examples:

#### EXAMPLE 1

20 6.2 kg of silicon tetrachloride are volatilised and mixed with 2.2 m<sup>3</sup> of hydrogen and 5.8 m<sup>3</sup> of air in the mixing chamber of a burner. The gas mixture burns from the outlet opening and is drawn by reduced pressure into the cooling system. After separation from the gas mixture containing hydrogen chloride, 2.2 kg of a highly disperse silica are obtained. It has a specific surface of 200 m<sup>2</sup>/g and a thickening effect in a polyester reference system of 3100 mPas (mpascal). 20

#### EXAMPLE 2

25 The procedure is the same as in Example 1 except that, in addition to the substances mentioned there, 0.5 kg/h of steam are introduced into the mixing chamber of the burner. The silica obtained has the specific surface of 466 m<sup>2</sup> and a thickening value of 3910 mPas. 25

#### EXAMPLE 3

30 The procedure is as in Example 1 except that 1.8 kg/h of steam are additionally introduced as described in Example 2. The silica obtained has a specific surface of 277 m<sup>2</sup>/g and a thickening value of 1040 mPas. 30

#### EXAMPLE 4

35 The procedure is as in Example 1 except that 0.5 kg/h of steam are introduced into the flame axis by probe at a distance of 1 cm from the outlet of the burner. The silica obtained has a specific surface of 309 m<sup>2</sup>/g and a thickening value of 4040 mPas. 35

#### EXAMPLE 5

40 The procedure is as described in Examples 1 and 4 except that 3 kg of steam are injected into the flame axis at a distance of 10 cm from the outlet opening of the burner. The silica obtained has BET-surface of 212 m<sup>2</sup>/g and a thickening value of 1105 mPas the measured values of the preceding Examples of the process according to the invention are summarised in Table I below. 40

The values for the specific surface and the thickening behaviour correspond to the curves b) in Figures 2 and 3.

TABLE I

Process according to the invention with  
additional introduction of steam

a) into the reaction mixture before combustion

b) into the Aerosil flame

Operational settings			steam input
SiCl <sub>4</sub> kg/h	H <sub>2</sub> m <sup>3</sup> /h	Air m <sup>3</sup> /h	kg/h
a) Into the reaction mixture before combustion:			
6.2	2.2	5.8	1.2
6.2	2.2	5.8	1.8
6.2	2.2	5.8	0.8
6.2	2.2	5.8	0.5
6.2	2.2	5.8	0.2
6.2	2.2	5.8	0.1
6.2	2.2	5.8	0.02
b) Into the Aerosil flame:			
6.2	2.2	5.6	0.8
6.2	2.2	5.6	2.0
6.2	2.2	5.6	3.0
6.2	2.2	5.6	0.5



TABLE 1

Process according to the invention with  
additional introduction of steam

a) into the reaction mixture before combustion

b) into the Aerosil flame

Surface	Thickening	Thickening based on standard
m <sup>2</sup> /g	m Pascal	%
<u>a) Into the reaction mixture before combustion:</u>		
391	2215	76
277	1040	36
441	2865	99
466	3910	135
226	3255	112
214	3060	106
196	3060	106
<u>b) Into the Aerosil flame:</u>		
348	3125	108
308	1605	58
212	1105	38
309	4040	139

#### CLAIMS

1. A process for the production of silica by the flame hydrolysis of a silicon-halogen compound in a flame formed by the combustion of a gas containing free or combined hydrogen in which an additional quantity of steam which does not result from the combustion of the hydrogen-containing gas is introduced into the reaction mixture.
2. A process as claimed in claim 1 wherein the additional steam is introduced into the mixing chamber of the burner through a separate pipe.
3. A process as claimed in claim 1 wherein the additional steam is introduced into the hydrogen-containing gas or oxygen-containing gas feed pipe leading to the burner.
4. A process as claimed in claim 3, wherein to mix them with steam, the hydrogen-containing gas or oxygen-containing gas is passed through a water evaporator at a temperature of from 20°C to the boiling temperature of the water.
5. A process as claimed in claim 1, wherein the additional steam is introduced directly into the flame where the silica is formed.
6. A process as claimed in any of claims 1 to 5 wherein the quantity of additional steam is from 0.1 to 1 kg of steam per kg of starting materials.
7. A process for the production of silica substantially as described with particular reference to any of Examples 2 to 5.
8. Silica when produced by a process as claimed in any of claims 1 to 7.